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(54)【発明の名称】 窒素酸化物接触還元用触媒

(57)【要約】

【構成】下記(1)式で表されるペロブスカイト型複合酸化物が固体酸担体に担持されてなる。



(式中、AはLaまたはCe、BはBa、Sr、Ca、Mg、Pb、ZnまたはAg、CはMn又はCo、CはFe、Ni、Cr、Cu、V、Mo、W、Ti、Zr、Nb、Pd、Rh、RuまたはPtであり、また $0 \leq X \leq 1$ 、 $0 \leq Y \leq 1$ である。)

【効果】工場、自動車などから排出される排ガスの中に含まれる有害な窒素酸化物、COおよび炭化水素を広いA/Fの範囲において効率良く浄化することができる。

【特許請求の範囲】

【請求項1】下記(1)式で表されるペロブスカイト型複合酸化物が固体酸担体に担持されてなることを特徴とする排ガス中の窒素酸化物、炭化水素化合物及び一酸化炭素を同時に除去するための触媒。

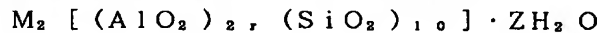


(式中、AはLaまたはCe、BはBa、Sr、Ca、Mg、Pb、Zn又はAg、CはMn又はCo、CはFe、Ni、Cr、Cu、V、Mo、W、Ti、Zr、Nb、Pd、Rh、Ru又はPtであり、また $0 \leq X \leq 1$ 、 $0 \leq Y \leq 1$ である。)

【発明の詳細な説明】

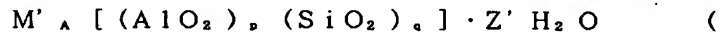
【産業上の利用分野】本発明は窒素酸化物接触還元用触媒に係わり、詳しくは工場、自動車などから排出される排ガスの中に含まれる有害な窒素酸化物、炭化水素及び一酸化炭素を同時に除去する際に使用する三元触媒に関する。

【従来の技術及び発明が解決しようとする課題】排ガス中の NO_x 、HC及びCOなどの有害成分を同時に除去する反応は NO_x を N_2 に還元する反応とHC及びCOを二酸化炭素と水に酸化する反応が同時に進行する反応であるため、排ガス中に含まれる酸素、 NO_x などの酸化性成分とHC、COなどの還元性成分の量比が極めて重要となるので、理論空燃比に近い条件で排ガス処理が行われている。しかし、理論空燃比での運転は燃費の悪化の一因となり、ウインドーの広い触媒の開発が望まれてきた。従来三元触媒成分として、白金-ロジウム、パラジウム-ロジウム、白金-パラジウム-ロジウム触媒が高い活性を示し、アルミナに白金-ロジウムを担持した触媒が実用化されている。また、これらの貴金属触媒は高価であるためこれに代わる触媒としてペロブスカイト型複合酸化物あるいはこれらにパラジウムを含有させる触媒などが提案されてきた。しかし、これらの触媒のいずれもが理論空燃比あるいはその近辺比でのみ高い活性を示した。(ウインドウの幅が狭い)そのため燃費を犠牲にすることなく幅の広いウインドウを有する触媒の開発が望まれてきた。本発明は、以上の事情に鑑みなされたものであって、その目的とするところは、幅の広いウインドウを有する三元触媒、言い換えれば理論空燃比*



(3)

(ただし、式中、Mはアルカリ金属イオン、rはゼオラ※ ※イトの合成条件により変動する値である。)



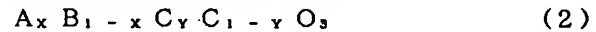
4)

(ただし、式中、イオンM'はアルカリ金属イオン、アルカリ土類金属イオン又は水素イオン、 $nA=p$ (nは、イオンMの価数である)、 $q/p \geq 5$ である。)

(ii) 酸化物系固体酸担体としては、 Al_2O_3 、 TiO_2 、 TiO_2/SO_4^{2-} 、 ZrO_2 、 ZrO_2/SO_4^{2-} 等の単一金属酸化物や、 SiO_2/Al_2O_3 、 TiO_2/Al_2O_3 、 TiO_2/ZrO_2 等の複

*からのずれが大きい排ガス条件下においても有効に機能する三元触媒を提供することにある。

【課題を解決するための手段】本発明に係る炭化水素及び/又は含酸素化合物を還元剤として使用する窒素酸化物接触還元用触媒は、下記(2)式で表されるペロブスカイト型複合酸化物が、ゼオライト、結晶性珪酸磷酸アルミニウム(SAPO)、結晶性磷酸アルミニウム(ALPO)、結晶性磷酸金属アルミニウム(MAPO)、アルミナ、チタニア、ジルコニア、シリカーアルミナ等の固体酸担体に担持されてなる。



(式中、AはLa又はCe、BはBa、Sr、Ca、Mg、Pb、Zn又はAg、CはMn又はCo、CはFe、Ni、Cr、Cu、V、Mo、W、Ti、Zr、Nb、Pd、Rh、RuまたはPtであり、また $0 \leq X \leq 1$ 、 $0 \leq Y \leq 1$ である。)本発明における固体酸担体とは、使用される温度領域において固体酸性を示す担体をいう。固体酸性の確認は、アンモニアを用いた昇温脱離法、あるいはアンモニア又はピリジンを用いたin situ FTIR法によりなされる。固体酸担体としては、次に示すゼオライト系固体酸担体や酸化物系固体酸担体などがある。

(i) ゼオライト系固体酸担体は、Na-モルデナイト、Na-ZSM-5、Na-USY (USY: ウルトラステイブルY型ゼオライト)等の耐熱性に優れるゼオライトを硫酸アンモニウム等のアンモニウム塩の水溶液又は硫酸等の酸で処理して、ゼオライト中のアルカリ金属の一部又は全部をアンモニウムイオン(NH_4^+)又は水素イオン(H^+)にイオン交換することにより得られる。 NH_4^+ でイオン交換する方法による場合は、最後に焼成処理を必要とする。ゼオライト系固体酸担体としては、例えば下記(3)式で表されるモルデナイト型ゼオライトを酸処理して得られる酸型モルデナイトであって、 SiO_2/Al_2O_3 のモル比が13~20であり、且つ、 SiO_2/Al_2O_3 のモル比が25~200である酸型モルデナイトや、下記(4)式で表されるゼオライト中のイオンMの一部又は全部を Ti^{4+} 、 Zr^{4+} 又は Sn^{4+} でイオン交換して得られるゼオライトが挙げられる。

3)、 TiO_2/Al_2O_3 、 TiO_2/ZrO_2 等の複合酸化物等が挙げられる。これらの中では、耐熱性の点で、 Al_2O_3 、 ZrO_2 、 SiO_2/Al_2O_3 が好ましい。

(iii) 固体酸担体の他の例としては、ゼオライト類似の多孔構造又は層状構造を有する一種の結晶性磷酸ア

ルミニウム (ALPO) や、その近縁物質である結晶性珪酸磷酸アルミニウム (SAPO)、ALPOの磷又は磷-アルミニウムの一部をチタン、鉄、マグネシウム、亜鉛、マンガン、コバルト等の金属で置換した結晶性磷酸金属アルミニウム (MAPO) などが挙げられる。ALPOタイプの磷酸塩は、上記の磷酸源及び金属源と、シリカ、シリカゾル、珪酸ソーダなどの中から選ばれた所望の組合せに、アミン、第四級アンモニウム等のいわゆるテンプレートと混合した原料から、ゼオライトを合成する場合と類似した条件下で水熱合成法により調整することが出来る。ゼオライトを合成する場合との主な相違点は、一般により高温 (概ね150℃以上) でpH酸性領域で合成されることである。ALPOタイプの磷酸塩の組成は、一般に $Al_2O_3 \cdot (0.8 \sim 1.2) \cdot P_2O_5 \cdot nH_2O$ で表される。また、SAPO又はMAPOの場合においては、置換するシリカ及び金属の最大量は、アルミニウム及び磷の総量の約1/10程度であるが、本発明においては、必ずしもこの組成範囲に入っていないもの、すなわち非晶質を含んでいるものを使用してもよい。水熱合成法により得られるALPOタイプの磷酸塩を担体として使用する場合は、一般に、水洗、乾燥した後、空气中で焼成して残存しているテンプレートを焼却除去したものが使用される。本発明に係る触媒は、例えば次に示す(1)、(2)又は(3)の方法により調整することができる。

(1) 固体酸担体を分散させたスラリー中に、La、Ce、Ba、Sr、Ca、Mg、Pb、Zn、Ag、Mn、Co、Fe、Ni、Cr、Cu、V、Mo、W、Ti、Zr、Nb、Pd、Rh、Ru又はPtの硝酸塩等の水溶性塩や、これらのアルコキシドにアルコール溶液を投入し、これらを中和あるいは加水分解させる方法などによって、固体酸担体にこれらの複合金属種の水酸化物等のペロブスカイト化合物前駆体を担持させる。次いで、濾過、水洗、リバルブを繰り返し行った後、乾燥し、焼成する。

(2) 固体酸担体と、別途調整したペロブスカイト化合物とを、遊星ミルなどによって十分に湿式粉碎混合する。

(3) 固体酸担体の水溶性塩又は水酸化物等の前駆体と、La、Ce、Ba、Sr、Ca、Mg、Pb、Zn、Ag、Mn、Co、Fe、Ni、Cr、Cu、V、Mo、W、Ti、Zr、Nb、Pd、Rh、Ru又はPtの硝酸塩等の水溶性塩や、これらのアルコキシドのアルコール溶液とを均質に混合した溶液を、中和又は加水分解させる方法などによって沈澱物を生成させる。次いで、この沈澱物を濾過、水洗、リバルブを繰り返し行った後、乾燥し、焼成する。以上の方法において、ペロブスカイト化合物の生成温度は低い方が好ましい。その理由は、その生成温度が低いほど、大きな比表面積を有するペロブスカイト化合物が得られ、固体酸担体と、ペロ

ブスカイト化合物を構成する元素との反応により固体酸担体の固体酸性が変質したり、ペロブスカイト化合物の生成量の低下により触媒の活性が低下したりすることを回避することができるからである。したがって、 Al_2O_3 、 TiO_2 などのようにペロブスカイト化合物を構成する元素との反応性が高い固体酸担体を用いる場合にあっては、固体酸担体を構成する元素とペロブスカイト化合物を構成する元素との均質性を高める(3)の方法は好ましくない。一般には、(1)の方法が好ましい

10 が、(2)の方法によってもかなり高い活性を示す触媒を得ることができる。ペロブスカイト化合物の好適な担持量は、このペロブスカイト化合物と固体酸担体との総重量に対して、1.0~50重量%である。50重量%を越えると、増量に応じた添加効果が得られないばかりでなく酸素が共存する反応系においては酸素による炭化水素や一酸化炭素の浄化率が高くなるものの NO_x の浄化率が大きく低下する。一方、1.0重量%未満では NO 、炭化水素、COのいずれの浄化率をも充分向上させることができない。本発明に係る触媒は、従来公知の成形方法によりハニカム状、球状等の種々の形状に成形することができる。この成形の際に、成形助剤、成形体補強体、無機繊維、有機バインダーなどを適宜配合してもよい。また、予め成形された基材上にウォッシュコート法などにより、被覆担持させることもできる。その他、従来公知の触媒調整法によることもできる。本発明に係る触媒が窒素酸化物、炭化水素及び一酸化炭素に対して浄化活性を示す最適な温度は、触媒種により異なるが、通常100~800℃であり、この温度領域においては、空間速度(SV)500~100,000程度で排ガスを通流させることが好ましい。なお、より好適な使用温度領域は200~800℃である。また本発明に係る触媒が有効に機能する空燃比(A/F)は、14.0~60であり、好ましくは14.0~40、より好ましくは14.0~30である。

【実施例】以下、本発明を実施例に基づいて更に詳細に説明するが、本発明は下記実施例に何ら限定されるものではなく、その要旨を変更しない範囲において適宜変更して実施することが可能なものである。

(1) 触媒の調整

40 実施例1

La(NO_3)₃・6H₂O、Mn(Ac)₂・4H₂O(Ac:CH₃COOH、以下も同じ)、Sr(NO_3)₂、Co(NO_3)₂・6H₂Oを、各々101.05g、28.60g、74.08g、135.83g秤量し、500mlの水に溶かした。この溶液に、充分に攪拌しながら121g/lのNaOH水溶液を加えて、pHを10とした。中和反応終了後、18時間攪拌を続け熱成を行った。その後、濾過、水洗、リバルブを、濾過水の導電率がリバルブ用水とほぼ同じになるまで繰り返した。得られた濾過ケーキを120℃で18時

間乾燥し、次いで700℃で3時間焼成した。得られた焼成物のXRDを求めた結果、ペロブスカイト結晶相が生成していることが判った。また、この焼成物のBET法による比表面積（以下の比表面積も同法による）は、 $23.7 \text{ m}^2/\text{g}$ であった（ $\text{La}_{0.4}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_3$ ）。このようにして得たペロブスカイト化合物30gと、硫酸法酸化チタン工程により得たメタチタン酸（ $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ）を600℃で3時間焼成して得た活性酸化チタン（比表面積： $104.2 \text{ m}^2/\text{g}$ ）100gとの混合物に、水100gを加え、遊星ミルにて30分間粉砕混合し、更に水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル（A-1）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.116gであった。

実施例2

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ と $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ とを、各々89.5g、50.66g秤量し、次いで、実施例1と同様の方法にて、ペロブスカイト化合物（ LaMnO_3 ）を得た。このペロブスカイト化合物の比表面積は、 $29.1 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、住友化学社製のγ-アルミナ100gとの混合物に、水100g加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、1.25mmピッチのハニカム形状の試作サンプル（A-2）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.094gであった。

実施例3

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Pb}(\text{NO}_3)_2$ 、 $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ を、各々71.60g、13.69g、50.66g秤量して混合し、次いで、800℃で3時間焼成したこと以外は実施例1と同様の方法にて、ペロブスカイト化合物（ $\text{La}_{0.4}\text{Pb}_{0.2}\text{MnO}_3$ ）を得た。このペロブスカイト化合物の比表面積は、 $23.7 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、住友化学社製のγ-アルミナ100gとの混合物に、水100g加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、1.25mmピッチのハニカム形状の試作サンプル（A-3）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.117gであった。

実施例4

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ を、各々88.07g、59.19g秤量して混合し、次いで、800℃で3時間焼成したこと以外は実施例1と同様の方法にて、ペロブスカイト化合物（ LaCoO_3 ）を得た。このペロブスカイト化合物の比表面積は、 $17.47 \text{ m}^2/\text{g}$ であった。このようにして得た

ペロブスカイト化合物30gと、日本化学社製のH形モルデナイト（HM-23）100gとの混合物に、水100g加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、1.25mmピッチのハニカム形状の試作サンプル（A-4）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.113gであった。

実施例5

$\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Ba}(\text{NO}_3)_2$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ を、各々70.65g、10.63g、59.19g秤量し、次いで実施例1と同様の方法にて、ペロブスカイト化合物（ $\text{Co}_{0.2}\text{Ba}_{0.2}\text{CoO}_3$ ）を得た。このペロブスカイト化合物の比表面積は、 $23.0 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、日本化学社製のH形モルデナイト（商品名「HM-23」）100gとの混合物に、水100g加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、1.25mmピッチハニカム形状の試作サンプル（A-5）を得た。このときのスラリーの塗布量はハニカム1cc当たり0.130gであった。

実施例6

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ 、 TiCl_4 水溶液（Tiとして14.82g/100ml濃度の水溶液）を、各々90.84g、25.71g、339.0ml秤量し、次いで、実施例1と同様の方法にて、ペロブスカイト化合物（ $\text{LaMn}_{0.8}\text{Ti}_{0.2}\text{O}_3$ ）を得た。このペロブスカイト化合物の比表面積は、 $25.3 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物10gと、日本アロジル社製のシリカ-アルミナ（商品名「COK-84」）100gとの混合物に、水100g加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、1.25mmピッチのハニカム形状の試作サンプル（A-6）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.098gであった。

実施例7

<ペロブスカイト化合物の調製>白水化学工業社製Laエトキシドのエタノール溶液（ La_2O_3 として73g/l濃度の溶液）、同社製のBaエトキシドのエタノール溶液（ BaO として79g/l濃度の溶液）、同社製Niエトキシドのエタノール溶液（ NiO として67g/l濃度の溶液）、Coエトキシドのエタノール溶液（ CoO として91g/l濃度の溶液）を、各々100.0ml、21.74ml、49.95ml、9.22ml秤量して混合し、充分攪拌しながら1重量%のアンモニア水溶液を徐々に滴下し加水分解させた。次いで、これを均一混合しながら蒸発乾固させ、600℃で3時間焼成してペロブスカイト化合物（ $\text{La}_{0.4}\text{Ba}_{0.2}\text{Co}_{0.2}\text{Ni}_{0.2}\text{O}_3$ ）を得た。このペロブ

スカイト化合物の比表面積は $36.9 \text{ m}^2/\text{g}$ であった。

<SAPO-34の調製>水 129.6 g に、攪拌しながら細かく砕いたアルミニウムイソプロポキシド 90.7 g を少量ずつ加え、均一になるまで攪拌混合した。この混合液に、 85% 磷酸水溶液 51.3 g を滴下し、均一になるまで攪拌混合した後、さらに 50% シリカゾル 16.0 g を加え、充分に攪拌混合した。次いで、水酸化テトラエチルアンモニウム 81.6 g を加え、充分に攪拌混合した。この混合物を、オートクレーブに仕込み、 200°C で 24 時間攪拌反応させた後、生成物を濾過分離し、さらに水洗、乾燥した後、 500°C で 3 時間空気中で焼成してSAPO-34を得た。このSAPO-34は、Si、Al、Pをそれぞれ 9.5 、 18.0 、 19.0 重量%含有する組成のものであった。このようにして得たペロブスカイト化合物 25 g と、 100 g のSAPO-34との混合物に、水 100 g を加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、 1.25 mm ピッチのハニカム形状の試作サンプル(A-7)を得た。このときのスラリーの塗布量は、ハニカム 1 cc 当たり 0.138 g であった。

実施例8

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Sr}(\text{NO}_3)_2$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{Fe}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ を、各々 101.05 g 、 74.08 g 、 135.83 g 、 33.60 g を秤量して混合し、実施例1と同様の方法にて、ペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.4}\text{Co}_{0.4}\text{Fe}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $21.6 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物 30 g と、住友化学社製の γ -アルミナ 100 g との混合物に、水 100 g を加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、 1.25 mm ピッチのハニカム形状の試作サンプル(A-8)を得た。このときのスラリーの塗布量は、ハニカム 1 cc 当たり 0.098 g であった。

実施例9

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ を、各々 202.10 g 、 28.41 g 、 135.83 g 、 28.19 g を秤量して混合し、実施例1と同様の方法にて、ペロブスカイト化合物($\text{La}_{0.4}\text{Zn}_{0.2}\text{Co}_{0.4}\text{Cu}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $17.3 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物 30 g と、住友化学社製の γ -アルミナ 100 g との混合物に、水 100 g を加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、 1.25 mm ピッチのハニカム形状の試作サンプル(A-9)を得た。このときのスラリーの塗布量は、ハニカム

1 cc 当たり 0.083 g であった。

実施例10

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 AgNO_3 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$ を、各々 202.10 g 、 19.82 g 、 135.83 g 、 69.87 g を秤量して混合し、実施例1と同様の方法にて、ペロブスカイト化合物($\text{La}_{0.4}\text{Ag}_{0.2}\text{Co}_{0.4}\text{Zr}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $17.3 \text{ m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物 30 g と、住友化学社製の γ -アルミナ 100 g との混合物に、水 100 g を加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、 1.25 mm ピッチのハニカム形状の試作サンプル(A-10)を得た。このときのスラリーの塗布量は、ハニカム 1 cc 当たり 0.097 g であった。

実施例11

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Sr}(\text{NO}_3)_2$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{Cr}(\text{NO}_3)_3$ を、各々 101.05 g 、 74.08 g 、 135.83 g 、 27.79 g を秤量して混合し、実施例1と同様の方法にて、ペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.4}\text{Co}_{0.4}\text{Cr}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $20.3 \text{ m}^2/\text{g}$ であった。

<ALPO-5の調製> 85% 磷酸 69.2 g と水 178 g との混合物に、擬ペーナイト粉末(アルミナ 67% 、酢酸 9.5% を含むもの) 45.8 g を少量ずつ加え、均一になるまで攪拌混合した。この液に、トリプロピルアミン 43.8 g を加え、均一になるまで攪拌混合した。この混合物をオートクレーブに仕込み、 150°C で 70 時間攪拌反応させた後、生成物を濾過分離し、水洗、乾燥した後、 500°C で 3 時間空気中で焼成してALPO-5を得た。このALPO-5は、Al、Pをそれぞれ 18.0 、 22.0 重量%含有する組成のものであった。このようにして得たペロブスカイト化合物 30 g と、 100 g のALPO-5との混合物に、水 100 g を加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、 1.25 mm ピッチのハニカム形状の試作サンプル(A-11)を得た。このときのスラリーの塗布量は、ハニカム 1 cc 当たり 0.104 g であった。

実施例12

<ペロブスカイト化合物の調製> $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Sr}(\text{NO}_3)_2$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 NbCl_5 (塩酸水溶液、Nbとして 50 g/l 濃度の溶液)を、各々 101.05 g 、 74.08 g 、 135.83 g 、 216.81 ml を秤量して混合し、以下実施例1にして、ペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.4}\text{Co}_{0.4}\text{Nb}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $18.9 \text{ m}^2/\text{g}$ で

あった。

<MAPO-5の調製>酢酸第一マンガン4.9gと酢酸第二銅4.1gとを水129gに溶解した液に攪拌しながら細かく砕いたアルミニウムイソプロポキシド56.3gを少量ずつ加え、均一になるまで攪拌混合した。この液に、85%磷酸55.4g、ジエチルエタノールアミン56.3g、水55.5gの混合液を攪拌しながら少量ずつ加え、均一になるまで攪拌混合した。この液をオートクレーブに仕込み、200℃で25時間反応させた後、生成物を濾過分離し、水洗、乾燥した後、500℃で3時間空気中で焼成してMAPO-5を得た。このMAPO-5は、Al、P、Mn、Cuをそれぞれ19.0、19.0、2.8、4.4重量%含有する組成のものであった。このようにして得たペロブスカイト化合物25gと、100gのMAPO-5との混合物に、水100g加えてスラリーを得、次いで実施例1と同様のハニカムに塗布して触媒を担持させ、1.25mmピッチのハニカム形状の試作サンプル(A-12)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.116gであった。

実施例13

実施例1において、活性化チタンに代えて水酸化ジルコニウムを600℃で3時間焼成して得たZrO₂（比表面積：148.3m²/g）を用いたこと以外は実施例1と同様にして試作サンプル(A-13)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.139gであった。

実施例14

<ペロブスカイト化合物の調製>La(NO₃)₃・6H₂O、Sr(NO₃)₂、Co(AC)₂・4H₂Oを、各々88.07g、10.76g、50.66g秤量し、500mlの水に溶かした。121g/lのNaOH水溶液を十分に攪拌しながら滴下して、液のpHを10とした。中和反応終了後、18時間攪拌を続け熟成を行った。その後、濾過、水洗、リバルブを、濾過水の導電率がリバルブ用水のそれとほぼ同じになるまで繰り返した後、濾過ケーキを120℃で18時間乾燥した。この乾燥物を粉碎し、この粉碎物にシュウ酸バナジル溶液(Vとして100g/l濃度の水溶液)25.90mlを加え充分混練した御蒸発乾固し、120℃で18時間乾燥し、次いで850℃で3時間焼成してペロブスカイト化合物(La_{0.8}Sr_{0.2}Co_{0.8}V_{0.2}O₃)を得た。このペロブスカイト化合物の比表面積は、12.8m²/gであった。〈シリカ-ジルコニアの調製〉

日産化学社製のシリカゾルO型(SiO₂として20重量%濃度のもの)と塩化ジルコニウム(ZrCl₄)を各々100.0g、97.20g秤量し攪拌しながら充分混合し、水にて総量を500mlとした。この液に、121g/lのNaOH水溶液を滴下し、pHを10と

した。中和反応終了後、18時間攪拌を続け、その後濾過、水洗、リバルブを繰り返して濾過ケーキを得、この濾過ケーキを120℃で18時間乾燥し、3時間焼成した。得られた焼成物の比表面積は、297m²/gであった。このようにして得られたペロブスカイト化合物30gと、上記焼成物100gとの混合物に、水100gを加え、遊星ミルにて30分間乾粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-14)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.127gであった。

実施例15

<ペロブスカイト化合物の調製>実施例14において、シュウ酸バナジル水溶液に代えてモリブデン酸アンモニウムのアンモニア性水溶液(MoO₃として25g/l濃度の水溶液)260.22mlを加えたこと以外は実施例14と同様にしてペロブスカイト化合物(La_{0.8}Sr_{0.2}Co_{0.8}Mo_{0.2}O₃)を得た。

<Zr-モルデナイトの調製>日本化学社製のNaモルデナイト(NM-100P)100gを硝酸ジルコニル水溶液(ZrO₂として100g/l濃度のもの)に浸漬し攪拌しながら70℃に1時間保持し、NaをZrとイオン交換させた。濾過、水洗して得たゼオライトケーキを乾燥後650℃で4時間焼成した。このゼオライト(Zr-モルデナイト)のZrの含有量は、3.3重量%であり、また比表面積は391m²/gであった。このようにして得たペロブスカイト化合物30gと、Zr-モルデナイト100gとの混合物に、水を100g加え、遊星ミルにて30分間粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-15)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.135gであった。

実施例16

実施例14において、シュウ酸バナジル水溶液に代えてメタタングステン酸アンモニウム水溶液(WO₃として50重量%の水溶液)23.58gを加えたこと以外は実施例14と同様にしてペロブスカイト化合物(La_{0.8}Sr_{0.2}Co_{0.8}Mo_{0.2}O₃)を得た。このペロブスカイト化合物の比表面積は、13.6m²/gであった。このようにして得たペロブスカイト化合物30gと、住友化学社製のγ-アルミナ(商品名「A-11」)100gとの混合物に、水を100g加え、遊星ミルにて30分間乾粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-16)を得た。このときのスラリーの塗布量は、ハニカム1cc

当たり0.135gであった。

実施例17

$\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Sr}(\text{NO}_3)_2$ 、 $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 、 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ を各々173.20g、126.98g、276.48g、25.90gを秤量し1000mlの水に溶かした。この水液に、121g/lの NaOH 水溶液攪拌しながら滴下し、 pH を10とした。加水分解反応終了後、18時間攪拌を続けた。以下実施例1と同様にして、ペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Pt}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $27.6\text{m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、住友化学社製の γ -アルミナ(商品名「A-11」)100gとの混合物に、水を100g加え、遊星ミルにて30分間粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-17)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.123gであった。

実施例18

実施例17において、 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ に代えて $\text{Rh}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ を16.25gを用いたこと以外は実施例17と同様の方法にして、ペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Rh}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $29.6\text{m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、住友化学社製の γ -アルミナ(商品名「A-11」)100gとの混合物に、水を100g加え、遊星ミルにて30分間粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-18)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.129gであった。

実施例19

実施例17において、 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ に代えて PdCl_2 を8.67gを用いたこと以外は実施例17と同様にして、ペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Pd}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $28.5\text{m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、住友化学社製の γ -アルミナ(商品名「A-11」)100gとの混合物に、水を100g加え、遊星ミルにて30分間粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-19)を

得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.122gであった。

実施例20

実施例17において、 $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ に代えて $\text{RuCl}_4 \cdot 5\text{H}_2\text{O}$ を16.15gを用いたこと以外は実施例17と同様にしてペロブスカイト化合物($\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Ru}_{0.2}\text{O}_3$)を得た。このペロブスカイト化合物の比表面積は、 $25.3\text{m}^2/\text{g}$ であった。このようにして得たペロブスカイト化合物30gと、住友化学社製の γ -アルミナ(商品名「A-11」)100gとの混合物に、水を100g加え、遊星ミルにて30分間粉碎混合し、さらに水で粘度調整してウォッシュコート用スラリーを得た。このスラリーを1.25mmピッチのコージュライト社製のハニカムに塗布して触媒を担持させ、試作サンプル(A-20)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.129gであった。

実施例21

実施例3において、ペロブスカイト化合物(LaCoO_3)と、日本化学社製のH型モルデナイト(商品名「HM-23」)とを、各々1g、100g使用したこと以外は実施例3と同様にして、1.25mmピッチのハニカム形状の試作サンプル(A-21)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.929gであった。

実施例22

実施例3において、ペロブスカイト化合物(LaCoO_3)と、日本化学社製のH型モルデナイト(商品名「HM-23」)とを、各々10g、100g使用したこと以外は実施例3と同様にして、1.25mmピッチのハニカム形状の試作サンプル(A-21)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.948gであった。

実施例23

実施例3において、ペロブスカイト化合物(LaCoO_3)と、日本化学社製のH型モルデナイト(商品名「HM-23」)とを、各々50g、100g使用したこと以外は実施例3と同様にして、1.25mmピッチのハニカム形状の試作サンプル(A-23)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.109gであった。

実施例24

実施例3において、ペロブスカイト化合物(LaCoO_3)と、日本化学社製のH型モルデナイト(商品名「HM-23」)とを、各々50g、100g使用したこと以外は実施例3と同様にして、1.25mmピッチのハニカム形状の試作サンプル(A-24)を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.122gであった。

実施例25

組成式： $\text{Na}_x[(\text{AlO}_2)_x \cdot (\text{SiO}_2)_y] \cdot \text{ZH}_2\text{O}$ で表されるナトリウム型モルデナイトの市販品（日本モービル社製、商品名「ZSM-5」、Y/X-35）100gを0.025モル/lの TiOSO_4 水溶液1リットル中に浸漬し、充分に攪拌した。これをオートクレーブ中にて攪拌しながら100℃/時の昇温速度で昇温して125℃に1時間保持し、 TiOSO_4 を加水分解させて、NaをTiでイオン交換した後、ろ別、水洗してゼオライトのケーキを得た。次いで、このケーキを乾燥した後、650℃で4時間焼成してゼオライトを得た。このゼオライト中のTiの含有量は TiO_2 として、2.4重量%であった。このようにして得たTi-ZSM-5をH型モルデナイトに代えて用いたこと以外は実施例3と同様にして、1.25mmビッチのハニカム形状の試作サンプル（A-25）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.110gであった。

比較例1

実施例1において、活性酸化チタンを使用せず、ペロブスカイト化合物（ $\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Mn}_{0.2}\text{O}_{3.2}$ ）

）だけを用いてウォッシュコート用スラリーを得、その他は実施例1と同様にして、1.25mmビッチのハニカム形状の比較サンプル（B-1）を得た。このときのスラリーの塗布量は、ハニカム1cc当たり0.132gであった。

(2) 評価試験

上記サンプル（A-1）～（A-25）並びに比較サンプル（B-1）について、下記の試験条件でA/Fを14.0～40の範囲を変化させることにより窒素酸化物COおよび C_xH_y 含有ガスの浄化試験を行った。

(試験条件)

(1) ガス組成 NO 1000ppm
CO 1%
 C_xH_y 1000ppm
CO₂ 10%
A/F 14～40

(2) 空間速度 10000 1/Hr

(3) 反応温度 300℃、400℃、500℃、又は600℃

結果を表1～表3に示す。

表 1

反応温度800℃

	A/F								
	14.6			20.0			40.0		
	NO	HC	CO	NO	HC	CO	NO	HC	CO
A-1	72	99	93	89	99	99	77	99	99
A-2	65	98	90	84	99	99	73	99	99
A-3	59	95	88	83	99	95	76	99	97
A-4	74	99	93	92	99	99	81	99	99
A-5	69	97	87	84	98	99	73	99	99
A-6	65	98	89	85	99	99	75	99	99
A-7	84	99	99	95	99	99	87	99	99
A-8	74	97	96	86	99	99	76	99	99
A-9	71	95	90	86	98	93	78	99	98
A-10	79	99	93	73	99	99	65	99	99
A-11	68	98	95	81	99	98	72	99	99
A-12	65	98	92	84	99	99	75	99	99
A-13	70	99	95	92	99	99	81	99	99

(表1つづき)

	14.6			20.0			40.0		
	NO	HC	CO	NO	HC	CO	NO	HC	CO
A-14	62	97	88	80	97	91	73	98	95
A-15	55	93	81	79	95	90	73	97	95
A-16	58	95	84	79	97	93	75	98	95
A-17	78	99	99	85	99	99	79	99	99
A-18	74	99	99	81	99	99	70	99	99
A-19	75	99	99	82	99	99	73	99	99
A-20	79	99	99	87	99	99	81	99	99
A-21	49	63	55	56	71	62	45	74	68
A-22	75	98	92	70	99	98	61	99	99
A-23	79	99	93	73	99	99	65	99	99
A-24	82	99	99	65	99	99	58	99	99
A-25	61	97	90	85	99	98	78	99	99
B-1	70	99	92	4	99	99	0	99	99

表 2

A/F=2.0における温度特性

触媒 A-4

300℃			400℃			500℃			600℃		
NO	HC	CO	NO	HC	CO	NO	HC	CO	NO	HC	CO
92	99	99	90	99	99	75	99	99	48	99	99

(11)

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*表1～表2より、本発明に係る触媒〔試作サンプル（A-1）～（A-25）〕は、いずれも窒素酸化物、CO及びC₂H₄の浄化率が高いのに対して、比較触媒〔比較サンプル（B-1）および（B-2）〕は、総じてその浄化率が低い事がわかる。

【発明の効果】以上詳細に説明したように、本発明に係る三元触媒は、広いA/Fの範囲において排ガス中の窒素酸化物CO、および炭化水素を効率良く浄化することができるなど、本発明は優れた特有の効果奏する。

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(54) CATALYST FOR CATALYTIC REDUCTION OF NITROGEN OXIDE**(57)Abstract:**

PURPOSE: To increase the purification efficiency of a ternary catalyst for simultaneous removal of NO_x, hydrocarbon compds. and CO in exhaust gas within a wide range of fuel-air ratio by supporting a perovskite type multiple oxide represented by a specified formula on a solid acid carrier.

CONSTITUTION: A perovskite type multiple oxide represented by a formula $A_xB_{1-x}C_yO_3$ is supported on zeolite or other solid acid carrier to obtain a catalyst for simultaneous removal of NO_x, hydrocarbon compds. and CO in exhaust gas. In the formula, A is La or Ce, B is Ba, Sr, Ca, Mg, Pb, Zn or Co, C is Fe, Ni, Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru or Pt, $0 \leq x \leq 1$ and $0 \leq y \leq 1$. When the catalyst is used, NO_x and hydrocarbon in exhaust gas are efficiently removed within a wide range of fuel-air ratio.

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JAPANESE

[JP,05-076762,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE

[Translation done.]

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3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] The catalyst for removing to coincidence the nitrogen oxides, hydrocarbon compound, and carbon monoxide in the exhaust gas characterized by solid acid support coming to support the perovskite mold multiple oxide expressed with following the (1) type.

AXB1-XCYC1-YO3 (1)

(Among a formula, La, or Ce and B are [Mn, or Co and C of Ba, Sr, calcium, Mg Pb, Zn, or Ag and C] Fe, nickel, Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, and A is $0 \leq X \leq 1$ and $0 \leq Y \leq 1$.)

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application] This invention relates to the three way component catalyst used in case the harmful nitrogen oxides contained in the exhaust gas discharged from works, an automobile, etc., a hydrocarbon, and a carbon monoxide are removed to coincidence in detail with respect to the catalyst for nitrogen-oxides catalytic reduction.

[Description of the Prior Art] Since the reactions which remove injurious ingredients in exhaust gas, such as NOX, HC, and CO, to coincidence are the reaction which returns NOX to N₂, and a reaction for which the reaction which oxidizes HC and CO in a carbon dioxide and water advances to coincidence and they become very important [the quantitative ratio of oxidizing quality components contained in exhaust gas, such as oxygen and NOX, and reducibility components such as HC and CO,], offgas treatment is performed on the conditions near theoretical air fuel ratio. However, operation by theoretical air fuel ratio became the cause of aggravation of fuel consumption, and development of a catalyst with a large window has been desired. Conventionally, as a three way component catalyst component, a platinum-rhodium-alloy, palladium-rhodium, and platinum-palladium-rhodium catalyst shows high activity, and the catalyst which supported the platinum rhodium alloy to the alumina is put in practical use. Moreover, since these precious metal catalysts are expensive, the catalyst which makes a perovskite mold multiple oxide or these contain palladium as a catalyst replaced with this has been proposed. however, any of these catalysts — although — only theoretical air fuel ratio or its neighborhood ratio showed high activity. (The width of face of a window is narrow) Therefore, development of the catalyst which has the window where width of face is wide has been desired, without sacrificing fuel consumption. This invention is made in view of the above situation, and the place made into the purpose is to offer the three way component catalyst which has the window where width of face is wide, and the three way component catalyst with which in other words the gap from theoretical air fuel ratio functions effectively on the bottom of a large exhaust gas condition.

[Means for Solving the Problem] Solid acid support, such as a zeolite, crystalline silicic acid aluminum phosphate (SAPO), crystalline aluminum phosphate (ALPO), crystalline phosphoric acid metal aluminum (MAPO), an alumina, a titania, a zirconia, and a silica alumina, comes to support the perovskite mold multiple oxide by which the catalyst for nitrogen-oxides catalytic reduction which uses the hydrocarbon and/or oxygenated compound concerning this invention as a reducing agent is expressed with following the (2) type. AXB₁-XCYC₁-YO₃ (2)

the inside of a formula, and A — La, or Ce and B — Ba, Sr, calcium, Mg, Pb, Zn, or Ag — C is Co, and Mn or C is Fe, nickel, Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, and it is $0 \leq X \leq 1$ and $0 \leq Y \leq 1$. The solid acid support in this invention means the support which shows solid acid nature in the temperature field used. The check of solid acid nature is in using the temperature programmed desorption which used ammonia, ammonia, or a pyridine. situ It is made by the FTIR method. As solid acid support, there are zeolite system solid acid support, oxide system solid acid support, etc. which are shown below.

(i) Zeolite system solid acid support processes the zeolite which is excellent in thermal resistance, such as Na-mordenite, Na-ZSM-5, and Na-USY (USY: ultra stay bull Y mold zeolite), from acids, such as a water solution of ammonium salt, such as an ammonium sulfate, or a sulfuric acid, and is obtained by carrying out the ion exchange of some or all of alkali metal in a zeolite to ammonium ion (NH₄⁺) or a hydrogen ion (H⁺). When based on the approach of carrying out the ion exchange by NH₄⁺, finally baking processing is needed. It is the acid type mordenite obtained by carrying out acid treatment of the mordenite mold zeolite expressed with following the (3) type, for example as zeolite system solid acid support. The acid type mordenite whose mole ratios of SiO₂/aluminum 2O₃ the mole ratios of SiO₂/aluminum 2O₃ are 13-20, and are 25-200, The zeolite obtained by carrying out the ion exchange of some or all of Ion M in the zeolite expressed with following the (4) type by Ti⁴⁺, Zr⁴⁺, or Sn⁴⁺ is mentioned.

M₂ [(AlO₂)₂ two r(SiO₂) 10] -ZH₂O (3)

(However, it is the value to which M is changed with alkali-metal ion among a formula, and r is changed according to the synthetic conditions of a zeolite.)

M'A [(AlO₂)_p(SiO₂)_q] -Z'H₂O (4)

(However, ion M' is alkali-metal ion, alkaline-earth-metal ion or a hydrogen ion, nA=p (n is the valence of Ion M), and q/p>=5 among a formula.)

(ii) — as oxide system solid acid support — aluminum₂ — O₃, TiO₂, TiO₂/SO₄, —, ZrO₂, and ZrO₂/SO₄ — single metallic oxides, such as —, the multiple oxide of SiO₂/aluminum 2O₃, TiO₂/aluminum 2O₃, and TiO₂/ZrO₂ grade, etc. are mentioned. In these, aluminum 2O₃ and SiO₂ [ZrO₂ and]/aluminum 2O₃ are desirable in respect of thermal resistance.

(iii) The crystalline aluminum phosphate (ALPO) of a kind which has the porous structure or the layer structure of zeolite resemblance as other examples of solid acid support, the crystalline phosphoric acid metal aluminum (MAPO) which permuted a part of crystalline silicic acid aluminum phosphate (SAPO) which is the close relationship matter, phosphorus of ALPO, or phosphorus-aluminum with metals, such as titanium, iron, magnesium, zinc, manganese, and cobalt, are mentioned. ALPO type phosphate can be adjusted to the combination of the request chosen from the above-mentioned phosphagen and the source of a metal, a silica and a silica sol, silicate of soda, etc. with a hydrothermal crystallization method under the case where a zeolite is compounded, and similar conditions, from the

raw material which mixed the so-called templates, such as an amine and quaternary ammonium. The main differences with the case where a zeolite is compounded are generally compounded more in pH acidity field by the elevated temperature (in general 150 degrees C or more). Generally the presentation of ALPO type phosphate is aluminum $2O_3$. $-(0.8-1.2)-$ It is expressed with P_2O_5 and nH_2O . Moreover, although the peaks of the silica which is permuted in SAPO or MAPO, and a metal are about 1 of the total amount of aluminum and phosphorus / 10, they may use in this invention what is not necessarily contained in this presentation range, i.e., the thing containing an amorphous substance. When using as support the phosphate of the ALPO type obtained by the hydrothermal crystallization method, after rinsing and drying, generally what carried out incineration removal of the template which calcinates and remains in air is used. The catalyst concerning this invention can be adjusted by the approach of (1), (2), or (3) shown below. In the slurry which distributed solid acid support, (1) La, Ce, Ba, Sr, calcium, Mg, Pb, Zn, Ag, Mn, Co, Fe, nickel, Cr, Cu, by water-soluble salts, such as a nitrate of V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, the method of throwing an alcoholic solution into these alkoxides and making these neutralize or hydrolyze, etc. Solid acid support is made to support perovskite compound precursors, such as these compound metal kinds of hydroxide. Subsequently, it dries and calcinates, after repeating filtration, rinsing, and repulping and performing them.

(2) Fully carry out wet-grinding mixing of solid acid support and the perovskite compound adjusted separately by a planetary mill etc.
 (3) Precursors, such as a water-soluble salt of solid acid support, or a hydroxide, and La, Ce, Ba, Sr, calcium, Mg, Pb, Zn, Ag, Mn, Co, Fe, nickel, Settling are made to generate by water-soluble salts, such as a nitrate of Cr, Cu, V, Mo, W, Ti, Zr, Nb, Pd, Rh, Ru, or Pt, the method of making the solution which mixed the alcoholic solution of these alkoxides to homogeneity neutralize or hydrolyze, etc. Subsequently, it dries and calcinates, after repeating filtration, rinsing, and repulping and performing these settling. In the above approach, the lower one of the generation temperature of a perovskite compound is desirable. The reason is that it is avoidable that the perovskite compound which has a big specific surface area is obtained, and the solid acid nature of solid acid support deteriorates by the reaction of solid acid support and the element which constitutes a perovskite compound, or the activity of a catalyst falls by the fall of the amount of generation of a perovskite compound, so that the generation temperature is low. therefore, aluminum₂ — if it is when using solid acid support with high reactivity with the element which constitutes a perovskite compound like O_3 and TiO_2 , the approach of (3) which raises the homogeneity of the element which constitutes solid acid support, and the element which constitutes a perovskite compound is not desirable. Generally, although the approach of (1) is desirable, the catalyst which shows quite high activity also by the approach of (2) can be acquired. The suitable amount of support of a perovskite compound is 1.0 – 50 % of the weight to the AUW of this perovskite compound and solid acid support. If 50 % of the weight is exceeded, although the rate of purification of a hydrocarbon or a carbon monoxide by oxygen becomes high in the system of reaction with which the addition effectiveness according to increase in quantity is not only acquired, but oxygen coexists, the rate of purification of NOX will fall greatly. On the other hand, at less than 1.0 % of the weight, NO, a hydrocarbon, and any rate of purification of CO cannot be raised enough. The catalyst concerning this invention can be conventionally fabricated in the shape of a honeycomb, and the various configurations of spherical ** by the well-known shaping approach. In the case of this shaping, a shaping assistant, a Plastic solid reinforcement object, an inorganic fiber, an organic binder, etc. may be blended suitably. Moreover, covering support can be carried out by the wash coat method etc. on the base material fabricated beforehand. In addition, it can also be conventionally based on the well-known catalyst preparation. Although the optimal temperature the catalyst concerning this invention indicates purification activity to be to nitrogen oxides, a hydrocarbon, and a carbon monoxide changes with catalyst kinds, it is usually 100–800 degrees C, and it is desirable in this temperature field to carry out conduction of the exhaust gas about (space-velocity SV) 500–100,000. In addition, a more suitable service temperature field is 200–800 degrees C. moreover, the air-fuel ratio (A/F) as which the catalyst concerning this invention functions effectively — 14.0–60 — it is — desirable — 14.0–40 — it is 14.0–30 more preferably.

[Example] It is possible to change this invention suitably in the range which is not limited to the following example at all and does not change the summary, and to carry out hereafter, although this invention is further explained to a detail based on an example.

(1) Respectively, 101.05g, 135.83g weighing capacity of adjustment example $1La(NO_3) \cdot 2.6H_2O$ of a catalyst, $Mn(Ac) \cdot 2.4H_2O$ (the same is said of $Ac:CH_3COOH$ and the following), $Sr(NO_3)_2$, and the $Co(NO_3) \cdot 2.6H_2O$ was carried out, and they were melted in 500ml water 74.08g 28.60g. The NaOH water solution of 121 g/l was added to this solution, fully stirring, and pH was set to 10. It riped by continuing stirring for 18 hours after neutralization termination. then, filtration, rinsing, and repulping — the conductivity of filtered water — repulping — it repeated until it became almost the same as service water. The obtained filter cake was dried at 120 degrees C for 18 hours, and, subsequently it calcinated at 700 degrees C for 3 hours. As a result of calculating XRD of the obtained baking object, it turned out that the perovskite crystal phase is generating. Moreover, the specific surface area (the following specific surface area is also depended on the law) by the BET adsorption method of this baking object was $23.7m^2/g$ ($La_{0.4}Sr_{0.6}Co_{0.8}Mn_{0.2}O_3$). Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of activity titanium oxide which calcinated the metatitanic acid (TiO_2 and H_2O) obtained according to the sulfuric-acid method titanium oxide process for 3 hours, and obtained it at 600 degrees C] (specific surface area: $104.2m^2/g$) mixture, in the planetary mill, grinding mixing was carried out for 30 minutes, viscosity control was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-1) was obtained. The coverage of the slurry at this time was 0.116g per honeycomb 1cc.

50.66g weighing capacity of example $2La(NO_3) \cdot 2.6H_2O$ and the 89.5g $Mn(Ac) \cdot 2.4H_2O$ was carried out respectively, and, subsequently the perovskite compound ($LaMnO_3$) was obtained by the same approach as Example I. The specific surface area of this perovskite compound was $29.1m^2/g$. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-2) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.094g per honeycomb 1cc.

50.66g weighing capacity of example $3La(NO_3) \cdot 2.6H_2O$, $Pb(NO_3)_2$, and the 71.60g $Mn(Ac) \cdot 2.4H_2O$ [13.69g] was carried out respectively, it mixed, and, subsequently the perovskite compound ($La_{0.8}Pb_{0.2}MnO_3$) was obtained by the same approach as Example I except having calcinated at 800 degrees C for 3 hours. The specific surface area of this perovskite compound was $23.7m^2/g$. Thus, in

addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-3) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.117g per honeycomb 1cc.

59.19g weighing capacity of example 4La(NO₃)₂·6H₂O and the 88.07g Co(NO₃)₂·6H₂O was carried out respectively, it mixed, and, subsequently the perovskite compound (LaCoO₃) was obtained by the same approach as Example 1 except having calcinated at 800 degrees C at 3:00. The specific surface area of this perovskite compound was 17.47m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and H form mordenite (HM-23) 100g [by the Japanization study company] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-4) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.113g per honeycomb 1cc.

59.19g weighing capacity of example 5Ce(NO₃)₂·6H₂O, Ba (NO₃)₂, and the 70.65g Co(NO₃)₂·6H₂O [10.63g] was carried out respectively, and, subsequently the perovskite compound (Co_{0.8}Ba_{0.2}CoO₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 23.0m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and H form mordenite (trade name "HM-23") 100g [by the Japanization study company] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-5) of 1.25mm pitch honeycomb configuration was obtained. The coverage of the slurry at this time was 0.130g per honeycomb 1cc.

339.0ml weighing capacity of example 6La(NO₃)₂·6H₂O, Mn(Ac)₂·4H₂O, and the 90.84g (water solution of 14.82g/100ml concentration as Ti) of the 25.71g of the TiCl₄ water solutions was carried out respectively, and, subsequently the perovskite compound (LaMn_{0.5}Ti_{0.5}O₃) was obtained by the same approach as Example 1. The specific surface area of this perovskite compound was 25.3m²/g. Thus, in addition to [100g of water] 10g of obtained perovskite compounds, and silica-alumina (trade name "COK-84") 100g [made from Japanese AROJIRU] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-6) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.098g per honeycomb 1cc.

The ethanol solution of La ethoxide by example 7 <preparation of perovskite compound> Hakusui Chemical Industries (solution of 73 g/l concentration as La₂O₃), 9.22ml weighing capacity is carried out and it mixes, and stirring enough, 1% of the weight of the aqueous ammonia solution was dropped gradually, and the ethanol solution (solution of 79 g/l concentration as BaO) of company Ba ethoxide, the ethanol solution (solution of 67 g/l concentration as NiO) of company nickel ethoxide, and 49.95ml (solution of 91g [l.] concentration as CoO) of 21.74ml of 100.0ml of ethanol solutions of Co ethoxide were made to hydrolyze respectively. Subsequently, evaporation to dryness was carried out, carrying out homogeneity mixing of this, it calcinated at 600 degrees C for 3 hours, and the perovskite compound (La_{0.8}Ba_{0.2}Co_{0.8}Ni_{0.2}O₃) was obtained. The specific surface area of this perovskite compound was 36.9m²/g.

Aluminum isopropoxide 90.7g broken finely was added to 129.6g of <preparation of SAPO-34> water small quantity every, stirring, and stirring mixing was carried out until it became homogeneity. 51.3g of phosphoric acid water solutions was dropped at this mixed liquor 85%, and after carrying out stirring mixing until it became homogeneity, stirring mixing was fully carried out [silica sol 16.0g] 50 more%. Subsequently, hydroxylation tetraethylammonium 81.6g was added and stirring mixing was fully carried out. After having carried out filtration separation of the product after it taught this mixture to the autoclave and it carried out the stirring reaction at 200 degrees C for 24 hours, and rinsing and drying further, it calcinated in 3-hour air at 500 degrees C, and SAPO-34 were obtained. These SAPO-34 were the thing of 9.5 and the presentation contained 18.0 or 19.0% of the weight about Si, aluminum, and P, respectively. Thus, 100g of water was added to the mixture of perovskite compounds [which were obtained / 25g and 100g] SAPO-34, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-7) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.138g per honeycomb 1cc. Weighing capacity of 101.05g, 74.08g, 135.83g, and the 33.60g was carried out respectively, example 8La(NO₃)₃·6H₂O, Sr (NO₃)₂, Co (NO₃)₂·6H₂O, and Fe(NO₃)₂·6H₂O were mixed, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Fe_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 21.6m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-8) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.098g per honeycomb 1cc.

Weighing capacity of 202.10g, 28.41g, 135.83g, and the 28.19g was carried out respectively, example 9La(NO₃)₃·6H₂O, Zn(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, and Cu(NO₃)₂ and 3H₂O were mixed, and the perovskite compound (La_{0.8}Zn_{0.2}Co_{0.8}Cu_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 17.3m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-9) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.083g per honeycomb 1cc.

Weighing capacity of 202.10g, 19.82g, 135.83g, and the 69.87g was carried out respectively, example 10La(NO₃)₃·6H₂O, AgNO₃, Co (NO₃)₂·6H₂O, and Zr(NO₃)₄ and 5H₂O were mixed, and the perovskite compound (La_{0.8}Ag_{0.2}Co_{0.8}Zr_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 17.3m²/g. Thus, in addition to [100g of water] 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] mixture, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-10) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.097g per honeycomb 1cc.

example 11La(NO₃)₃·6H₂O — O, Sr (NO₃)₂, and Co(NO₃)₂·6H₂O — weighing capacity of each 101.05g, 74.08g, 135.83g, and 27.79g was

carried out, O and Cr (NO₃)₃ were mixed, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Cr_{0.2}O₃) was obtained by the same approach as an example 1. The specific surface area of this perovskite compound was 20.3m²/g.

45.8g (what contains 9.5% of acetic acids alumina 67%) of pseudo-boehmite powder was added to 69.2g of phosphoric acid, and 178g [of water] mixture small quantity every <preparation of ALPO-5> 85%, and stirring mixing was carried out until it became homogeneity. Tripropylamine 43.8g was added to this liquid, and stirring mixing was carried out until it became homogeneity. After teaching this mixture to the autoclave and carrying out a stirring reaction at 150 degrees C for 70 hours, filtration separation of the product was carried out, after rinsing and drying, it calcinated in 3-hour air at 500 degrees C, and ALPO-5 were obtained. These ALPO-5 were the thing of the presentation which contains aluminum and P 18.0 or 22.0% of the weight, respectively. Thus, in addition to [100g of water] the mixture of perovskite compounds [which were obtained / 30g and 100g] ALPO-5, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-11) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.104g per honeycomb 1cc.

216.81ml weighing capacity of the 74.08g 101.05g [135.83g] was carried out respectively, it mixed, example 12 <preparation of perovskite compound> La(NO₃)₂·6H₂O, Sr (NO₃)₂, Co(NO₃)₂·6H₂O, and NbCl₅ (a hydrochloric-acid water solution, solution of 50 g/l concentration as Nb) were made into the example 1 below, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Nb_{0.2}O₃) was obtained. The specific surface area of this perovskite compound was 18.9m²/g.

Stirring mixing was carried out until it added aluminum iso prop KISHIDO 56.3g broken finely small quantity every and became homogeneity, stirring first manganese of <preparation of MAPO-5> acetic acid 4.9g, and 4.1g of cupric acetate in the liquid which dissolved in 129g of water. Stirring mixing was carried out until it became homogeneity in this liquid [small quantity every], stirring 55.4g [of phosphoric acid], and diethyl ethanolamine 56.3g, and the mixed liquor of 55.5g of water 85%. After teaching this liquid to the autoclave and making it react at 200 degrees C for 25 hours, filtration separation of the product was carried out, after rinsing and drying, it calcinated in 3-hour air at 500 degrees C, and MAPO-5 were obtained. These MAPO-5 were the thing of 19.0, 19.0, and the presentation contained 2.8 or 4.4% of the weight about aluminum, P, Mn, and Cu, respectively. Thus, in addition to [100g of water] the mixture of perovskite compounds [which were obtained / 25g and 100g] MAPO-5, the slurry was obtained, subsequently applied to the same honeycomb as an example 1, the catalyst was made to support, and the prototype sample (A-12) of the honeycomb configuration of 1.25mm pitch was obtained. The coverage of the slurry at this time was 0.116g per honeycomb 1cc.

In example 13 example 1, it replaced with activity titanium oxide and the prototype sample (A-13) was obtained like the example 1 except having used ZrO₂ (specific surface area: 148.3m²/g) which calcinated zirconium hydroxide for 3 hours and obtained it at 600 degrees C. The coverage of the slurry at this time was 0.139g per honeycomb 1cc.

Respectively, 88.07g, 50.66g weighing capacity of example 14 <preparation of perovskite compound> La(NO₃)₂·6H₂O, Sr (NO₃)₂, and the Co(Ac)₂·4H₂O was carried out, and they were melted in 500ml water 10.76g. It was dropped fully stirring the NaOH water solution of 121 g/l, and pH of liquid was set to 10. It riped by continuing stirring for 18 hours after neutralization termination. then, filtration, rinsing, and RIPARUBU — the conductivity of filtered water — RIPARUBU — after repeating until it became almost the same as it of service water, the filter cake was dried at 120 degrees C for 18 hours. this dry matter was ground, 25.90ml (water solution of 100 g/l concentration as V) of oxalic acid vanadyl solutions was added to this grinding object, and it kneaded enough — evaporation to dryness was carried out, and it dried at 120 degrees C for 18 hours, subsequently it calcinated at 850 degrees C for 3 hours, and the perovskite compound (La_{0.8}Sr_{0.2}Co_{0.8}V_{0.2}O₃) was obtained. The specific surface area of this perovskite compound was 12.8m²/g. It mixed enough, having carried out 97.20g weighing capacity of the 100.0g of the silica sol O molds (thing of 20-% of the weight concentration as SiO₂) and zirconium chlorides (ZrCl₄) by the preparation > Nissan chemistry company of a <silica-zirconia, and stirring them respectively, and the total amount was set to 500ml with water. The NaOH water solution of 121 g/l was dropped at this liquid, and pH was set to 10. Stirring was continued after neutralization termination for 18 hours, filtration, rinsing, and RIPARUBU were repeated after that, the filter cake was obtained, at 120 degrees C, it dried for 18 hours and this filter cake was calcinated for 3 hours. The specific surface area of the obtained baking object was 297m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of the above-mentioned baking objects] mixture, ***** mixing during 30 minutes was carried out in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-14) was obtained. The coverage of the slurry at this time was 0.127g per honeycomb 1cc.

In the example 15 <preparation of perovskite compound> example 14, the perovskite compound (La_{0.8}Sr_{0.2}Co_{0.8}Mo_{0.2}O₃) was obtained like the example 14 except having replaced with the oxalic acid vanadyl water solution, and having added 260.22ml (water solution of 25 g/l concentration as MoO₂) of ammonia nature water solutions of an ammonium molybdate.

It held at 70 degrees C for 1 hour, having been immersed in the zirconium nitrate water solution (referred to as ZrO₂ thing of 100 g/l concentration), and stirring Na mordenite (NM-100P) 100g by the <preparation of Zr-mordenite> Japanization study company, and the ion exchange of Na was carried out to Zr. It calcinated at 650 degrees C after drying the zeolite cake rinsed [was filtered and] and obtained for 4 hours. The content of Zr of this zeolite (Zr-mordenite) was 3.3 % of the weight, and specific surface area was 391m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and Zr-mordenite 100g mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-15) was obtained. The coverage of the slurry at this time was 0.135g per honeycomb 1cc.

In example 16 example 14, the perovskite compound (La_{0.8}Sr_{0.2}Co_{0.8}Mo_{0.2}O₃) was obtained like the example 14 except having replaced with the oxalic acid vanadyl water solution, and having added 23.58g (50% of the weight of water solution as WO₃) of ammonium metatungstate water solutions. The specific surface area of this perovskite compound was 13.6m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, ***** mixing was carried out in the planetary mill for 30 minutes, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-16) was obtained. The coverage of the slurry at this time was 0.135g per honeycomb

1cc.

Respectively, weighing capacity of 173.20g, 126.98g, 276.48g, and the 25.90g was carried out, and example 17La(NO₃)₃·6H₂O, Sr(NO₃)₂, Co(NO₃)₂·6H₂O, and H₂PtCl₆·6H₂O were melted in 1000ml water. While 121 g/l carried out NaOH water-solution stirring, it was dropped at this water, and pH was set to 10. Stirring was continued after hydrolysis reaction termination for 18 hours. The perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Pt_{0.05}O₃) was obtained like the example 1 below. The specific surface area of this perovskite compound was 27.6m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-17) was obtained. The coverage of the slurry at this time was 0.123g per honeycomb 1cc.

In example 18 example 17, it replaced with H₂PtCl₆·6H₂O, and Rh(NO₃)₃·2H₂O was made into the same approach as an example 17 except having used 16.25g, and the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Rh_{0.05}O₃) was obtained. The specific surface area of this perovskite compound was 29.6m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-18) was obtained. The coverage of the slurry at this time was 0.129g per honeycomb 1cc.

In example 19 example 17, the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Pd_{0.05}O₃) was obtained like the example 17 except having replaced with H₂PtCl₆·6H₂O, and having used 8.67g for PdCl₂. The specific surface area of this perovskite compound was 28.5m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-19) was obtained. The coverage of the slurry at this time was 0.122g per honeycomb 1cc.

In example 20 example 17, the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.95}Ru_{0.05}O₃) was obtained like the example 17 except having replaced with H₂PtCl₆·6H₂O, and having used 16.15g for RuCl₄ and 5H₂O. The specific surface area of this perovskite compound was 25.3m²/g. Thus, 100g of water was added to 30g of obtained perovskite compounds, and 100g [of gamma-alumina by Sumitomo Chemical Co., Ltd.] (trade name "A-11") mixture, grinding mixing was carried out for 30 minutes in the planetary mill, viscosity preparation was carried out further with water, and the slurry for wash coats was obtained. Applied this slurry to the honeycomb by the KOJU light company of 1.25mm pitch, the catalyst was made to support, and the prototype sample (A-20) was obtained. The coverage of the slurry at this time was 0.129g per honeycomb 1cc.

In example 21 example 3, the prototype sample (A-21) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except ** which used a perovskite compound (LaCoO₃) and 1g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.929g per honeycomb 1cc.

In example 22 example 3, the prototype sample (A-21) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having used a perovskite compound (LaCoO₃) and 10g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.948g per honeycomb 1cc.

In example 23 example 3, the prototype sample (A-23) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having used a perovskite compound (LaCoO₃) and 50g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.109g per honeycomb 1cc.

In example 24 example 3, the prototype sample (A-24) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having used a perovskite compound (LaCoO₃) and 50g (trade name "HM-23") of 100g of H mold mordenites by the Japanization study company respectively. The coverage of the slurry at this time was 0.122g per honeycomb 1cc.

Example 25 empirical formula: It was immersed into 1l. of 0.025 mols [/l.] TiOSO₄ water solutions, and 100g (made in Japanese Mobile, a trade name "ZSM-5", Y/X -35) of commercial items of the sodium mold mordenite expressed with Na_x[(AlO₂)_x and (SiO₂)_y], and ZH₂O was fully stirred. After having carried out the temperature up with the programming rate of 100 degrees C/o'clock, having held at 125 degrees C for 1 hour, making TiOSO₄ hydrolyze and carrying out the ion exchange of Na by Ti, stirring this in an autoclave, the ** exception, it rinsed and the cake of a zeolite was obtained. Subsequently, after drying this cake, it calcinated at 650 degrees C for 4 hours, and the zeolite was obtained. The content of Ti in this zeolite was 2.4 % of the weight as TiO₂. Thus, the prototype sample (A-25) of the honeycomb configuration of 1.25mm pitch was obtained like the example 3 except having replaced with and used obtained Ti-ZSM-5 for H mold mordenite. The coverage of the slurry at this time was 0.110g per honeycomb 1cc.

In example of comparison 1 example 1, activity titanium oxide was not used, but the slurry for wash coats was obtained only using the perovskite compound (La_{0.4}Sr_{0.6}Co_{0.8}Mn_{0.2}O₃), and others obtained the comparison sample (B-1) of the honeycomb configuration of 1.25mm pitch like the example 1. The coverage of the slurry at this time was 0.132g per honeycomb 1cc.

(2) The purification trial of nitrogen oxides CO and C₃H₆ content gas was performed by A/F changing the range of 14.0-40 to the evaluation test above-mentioned sample (A-1) - (A-25) a list by the following test condition about a comparison sample (B-1).

(Test condition)

(1) Gas presentation NO 1000ppmCO 1%C₃H₆ 1000ppmCO₂ 10%A/F 14-40 (2) space velocity 10000 l/Hr (3) reaction temperature 300 degrees C, 400 degrees C, 500 degrees C, or 600-degree-C result is shown in Table 1 - 3.

表 1

反応温度 800℃

	A/F								
	14.6			20.0			40.0		
	NO	HC	CO	NO	HC	CO	NO	HC	CO
A-1	72	99	93	89	99	99	77	99	99
A-2	65	98	90	84	99	99	73	99	99
A-3	59	95	88	83	99	95	76	99	97
A-4	74	99	93	92	99	99	81	99	99
A-5	69	97	87	84	98	99	73	99	99
A-6	65	98	89	85	99	99	75	99	99
A-7	84	99	99	95	99	99	87	99	99
A-8	74	97	96	86	99	99	76	99	99
A-9	71	95	90	86	98	93	78	99	98
A-10	79	99	93	73	99	99	65	99	99
A-11	68	98	95	81	99	98	72	99	99
A-12	65	98	92	84	99	99	75	99	99
A-13	70	99	95	92	99	99	81	99	99

(表1つづき)

	14.6			20.0			40.0		
	NO	HC	CO	NO	HC	CO	NO	HC	CO
A-14	62	97	88	80	97	91	73	98	95
A-15	55	93	81	79	95	90	73	97	95
A-16	58	95	84	79	97	93	75	98	95
A-17	78	99	99	85	99	99	79	99	99
A-18	74	99	99	81	99	99	70	99	99
A-19	75	99	99	82	99	99	73	99	99
A-20	79	99	99	87	99	99	81	99	99
A-21	49	63	55	56	71	62	45	74	68
A-22	75	98	92	70	99	98	61	99	99
A-23	79	99	93	73	99	99	65	99	99
A-24	82	99	99	65	99	99	58	99	99
A-25	61	97	90	85	99	98	78	99	99
B-1	70	99	92	4	99	99	0	99	99

表 2

A/F=20における温度特性

触媒 A-4

300℃			400℃			500℃			600℃		
NO	HC	CO	NO	HC	CO	NO	HC	CO	NO	HC	CO
92	99	99	90	99	99	75	99	99	48	99	99

From Table 1 - 2, the catalyst [prototype sample (A-1) concerning this invention - (A-25)] all understand that the rate of purification is low generally to a thing with high nitrogen oxides, CO, and rate of purification of C₃H₆ for a comparison catalyst [comparison sample (B-1) and (B-2)].

[Effect of the Invention] As explained to the detail above, this invention does the outstanding characteristic effectiveness so — the three way component catalyst concerning this invention can purify efficiently the nitrogen oxides CO and the hydrocarbon in exhaust gas in the range of large A/F.

[Translation done.]

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